Revised Hydrocarbon Solvent Bin MIR Calculation

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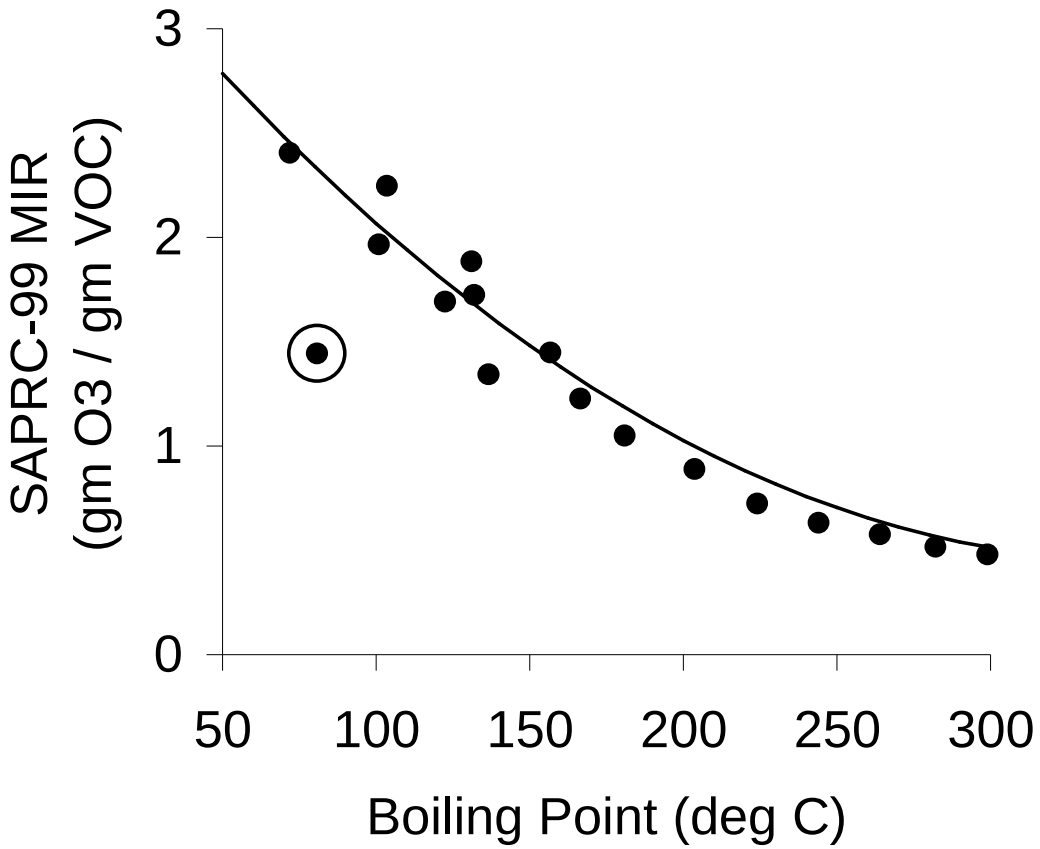
Outline

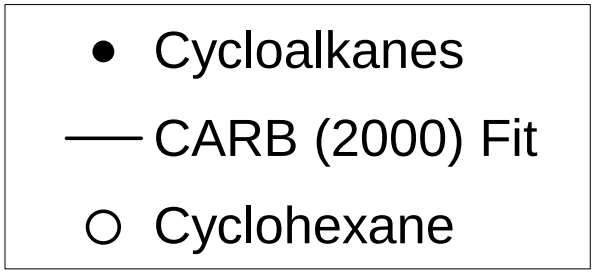
- CARB bins for assigning MIRs for hydrocarbon solvents
- Revised hydrocarbon bin reactivity estimation method
- Evaluation of bin reactivity estimation methods
- Update of bin MIRs to SAPRC-07

CARB Bins for Hydrocarbon Solvents

- Hydrocarbon solvents are used in many applications. MIR values are needed for CARB reactivity-based regulations
- Many hydrocarbon solvent reactivities are difficult to calculate because they are complex mixtures of alkanes and aromatics whose exact compositions are unknown
- The CARB derived a “Bin” method for estimating HC solvent MIRs for the aerosol coatings regulation (Kwok et al., 2000)
  - CARB created 24 hydrocarbon “bins” based on alkane and aromatic type fractions and boiling point ranges
  - SAPRC-99 MIR vs. boiling point correlations for each type fraction (n-, iso- and cycloalkanes and aromatics) were used to assign a SAPRC-99 MIR for each bin

Example of Boiling Point vs. MIR fits: Cycloalkane MIRs vs. Boiling Point





Cyclohexane does not fall on the curve so its MIR is overestimated by this method.

This affects MIR estimates for light hydrocarbon mixtures.

CARB Hydrocarbon Bins

Bin	1-5	6-10	10-15	16-20
Boiling Point Range (deg F)	80-205	>205-340	>340-460	>460-580
	Assigned SAPRC-99 MIR			
Alkanes (< 2% Aromatics)	2.08	1.41	0.91	0.57
N- & Iso-Alkanes (< 2% Aromatics)	1.59	1.17	0.81	0.51
Cyclo-Alkanes (< 2% Aromatics)	2.52	1.65	1.01	0.63
Alkanes (2 to < 8% Aromatics)	2.24	1.62	1.21	0.88
Alkanes (8 to 22% Aromatics)	2.56	2.03	1.82	1.49
Bin	21	22	23	24
Boiling point range	280-290	320-350	355-420	450-535
	Assigned SAPRC-99 MIR			
Aromatic Content (<98%)	7.37	7.51	8.07	5.00

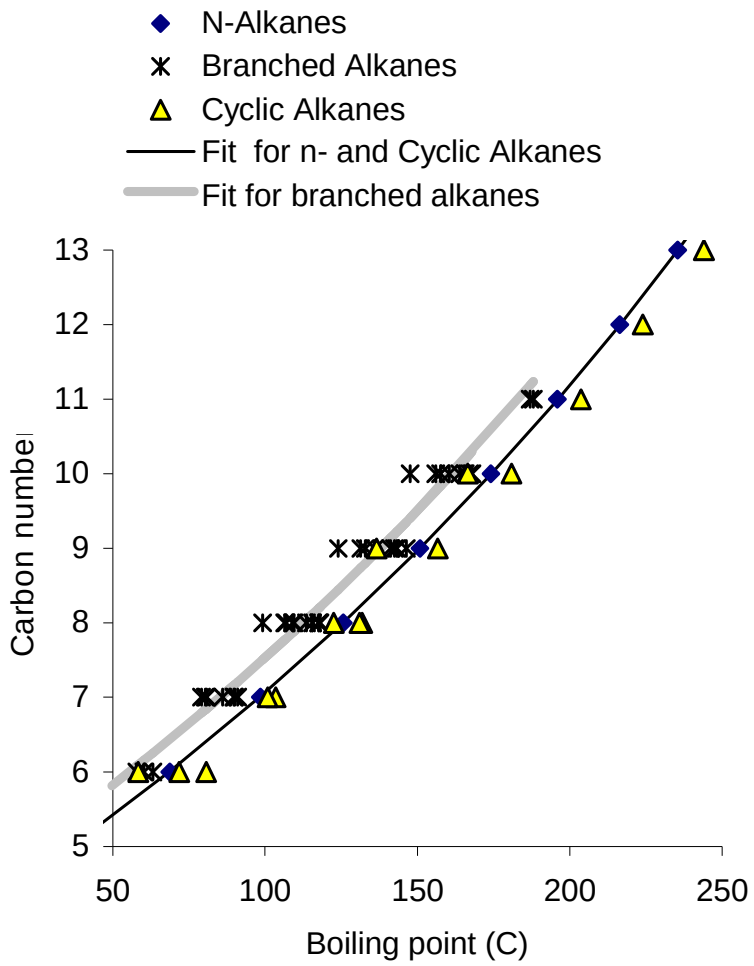
Problems with ARB Bin MIR Estimation Method

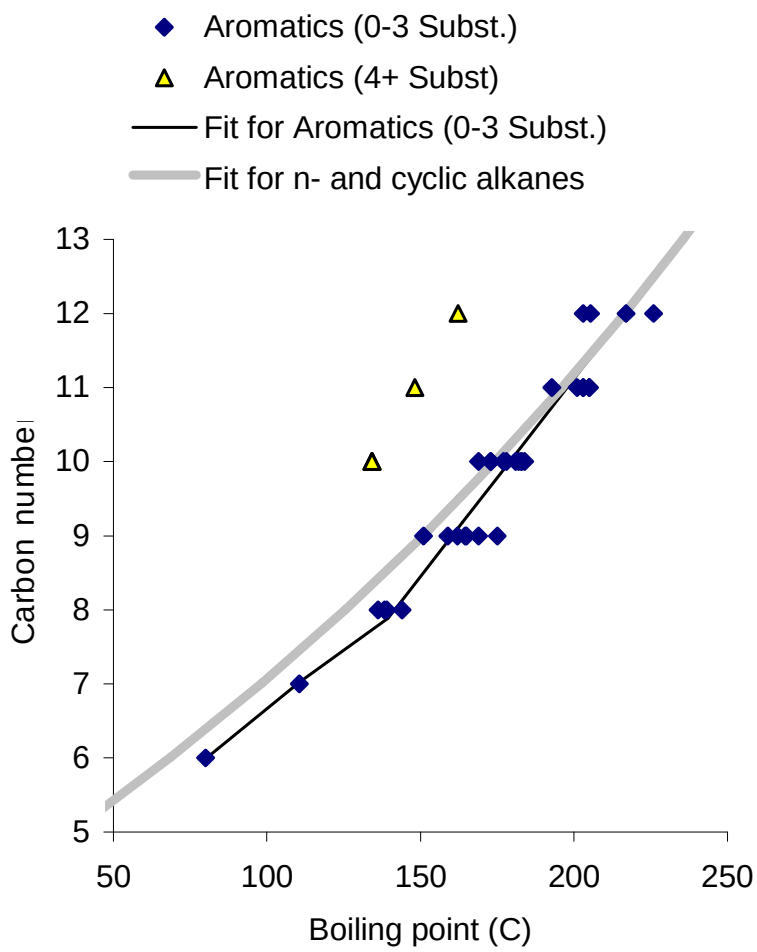
- Compositions of hydrocarbon solvents used to derive and evaluate the CARB method are not available due to confidentiality concerns
- CARB method may overestimate MIRs for light hydrocarbon solvents containing significant amounts of cyclohexane
- Not straightforward to obtain reactivities in other scales, or when the MIR scale is updated (e.g., to SAPRC-07)

Revised Hydrocarbon Bin Reactivity Estimation Method

- Derive a speciation composition for each bin, then use the component reactivities to calculate reactivities in any scale
- This involves:
  - Assigning specific alkane type and aromatic fractions and boiling point distributions for each bin.
  - Estimating carbon number distributions for each boiling range.
  - Assigning specific compounds (or SAPRC lumped molecule groups) for each hydrocarbon type and carbon number
- Assumptions:
  - Alkane type fractions (n-, iso-, and cyclo-) are equally distributed if not specified
  - Boiling point distributions are the same for each HC type
  - Compositions of each HC type depend only on carbon no.

Carbon Numbers vs. Boiling Points





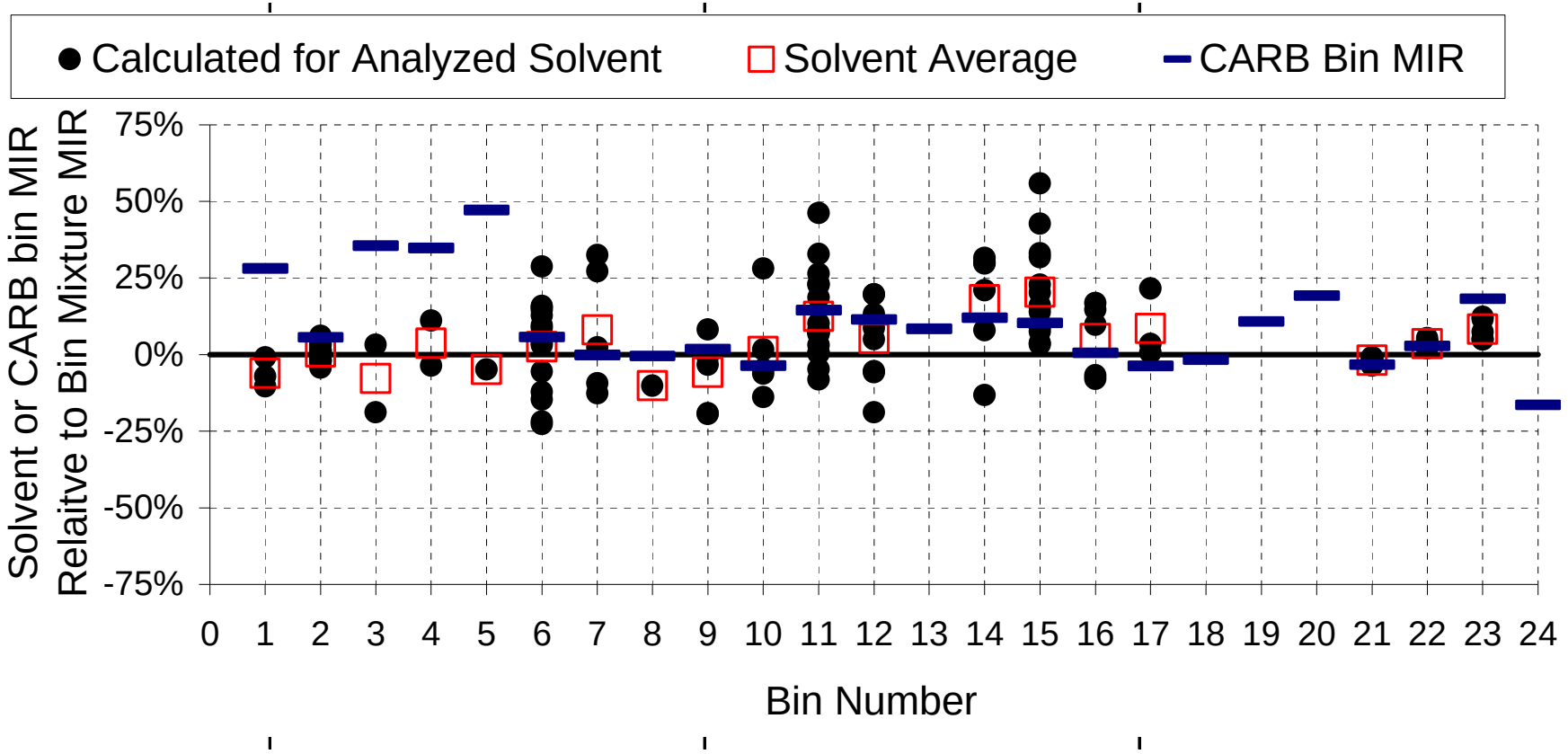
Derivation of Compositions for Hydrocarbon Types and Carbon Numbers

- Normal alkanes: single compound for each carbon number
- Branched and cyclic alkanes: Use SAPRC isomeric mixture groups BR-Cn and CYC-Cn
  - Sets of representative compounds have already been chosen for each carbon number
  - C_6 cyclic alkanes assumed to be primarily cyclohexane
- Aromatics: representative compositions derived for each carbon number based on analyses of 41 aromatic-containing solvents
  - Data from Censullo et al (2002),the ACC (Jaques, 2004) and solvents analyzed for various reactivity projects at UCR.
  - Although compositions varied, aromatic MIRs for a given carbon number were fairly consistent for the 41 solvents
  - Minimum carbon number used was 6.5 (benzene + toluene)

Evaluation of Bin MIR Calculation Methods

- MIRs assigned to each bin are compared with MIRs calculated explicitly for 124 solvents with sufficient compositional data
  - Data from Censullo et al (2002),the ACC (Jaques, 2004) and solvents analyzed for various reactivity projects at UCR.
  - All had distributions of n-, iso-, and cycloalkanes given for each carbon no. and speciated aromatic data (if applicable)
  - 19 of the 24 bins represented
- Analyzed solvent MIRs are compared with bin MIRs assigned by the CARB (Kwok et al. 2000) and calculated for SAPRC-99 from the assigned bin compositions (this work)
- Generally good agreement obtained between solvent and bin MIRs except the CARB method overestimates MIRs for the light hydrocarbon bins with cycloalkanes (bins 1,3,4, and 5).

Analyzed Solvent and CARB Bin MIRs vs. Bin MIRs Calculated from Compositions

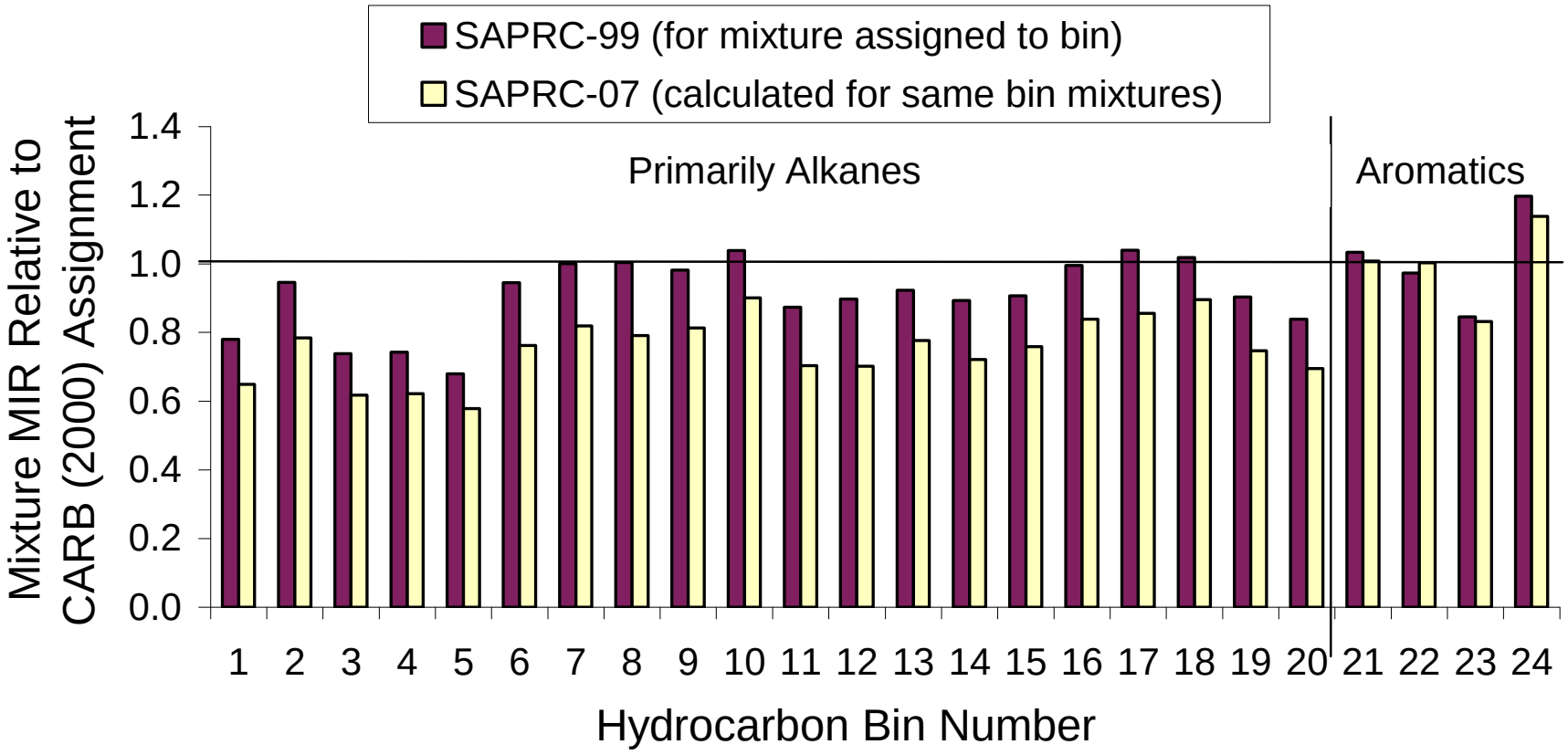


- Solvent and bin mixture MIRs calculated using SAPRC-99
- CARB Bin MIR from Kwok et al (2000)

Update of Bin MIRs to SAPRC-07

- The bin composition assignments are used to update the bin MIRs to SAPRC-07
- Note that the updated bin MIRs reflect both a change in method as well as a change in mechanism
  - Change in mechanism: MIRs for alkane bins (1-20) decrease by ~20%
  - Change in method: MIRs decrease even more for the light carbon with cycloalkane bins 1 and 3-5.
  - MIR changes in aromatic bins 21-24 are relatively small

Change in Bin MIRs Caused by Method and Mechanism Update



Summary and Conclusions

- A revised method to derive hydrocarbon bin reactivities based on estimating compositions for each bin was developed
- The method performs as well or better than the CARB (2000) method for predicting MIRs of analyzed solvents
- The revised method should be appropriate for use for regulatory reactivity scale updates
- The revised method was used to derive bin MIRs for the SAPRC-07 reactivity scale